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The Analysis of Complex Alloys of
the Nickel, Copper, Chromium Type

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THE ANALYSIS OF COMPLEX ALLOYS OF THE
NICKEL, COPPER, CHROMIUM TYPE

BY

SILAS ALONZO BRALEY
A. B. Morningside College, 1913

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

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June 3, 1915

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY Silas Alonzo Braley
ENTITLED THE ANALYSIS OF COMPLEX ALLOYS OF THE
NICKEL, COPPER, CHROMIUM TYPE
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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In Charge of Thesis

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Recommendation concurred in:*

_____ } Committee
on
Final Examination*

*Required for doctor's degree but not for master's.

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THE ANALYSIS OF COMPLEX ALLOYS OF THE NICKEL, COPPER, CHROMIUM TYPE

Introduction and Purpose of the Investigation.

The new alloy of the nickel, copper, chromium type as prepared by Professor S. W. Parr of the University of Illinois*

* Eighth Int. Congress of App. Chem., Pt. 2, p.209)

has met many of the requirements for which it was intended. It is extremely resistant to acids and atmospheric corrosion, has great tensile strength and withstands high temperatures. But because of its extreme hardness it cannot be successfully machined, hammered, drawn or spun. Therefore, to make it a success, alteration of the composition becomes necessary.

To prepare the alloy, a charge is made up of the pure metals or of their various alloys, placed in a crucible and the whole heated to a temperature of about 1500°C. At some time during the process some de-oxidizing agent is added and also some material to free the charge of occluded gases.

It is a well known fact that many metals will volatilize appreciably when heated to such high temperatures. This together with the losses caused by the slagging off of part of the charge, to the action of the charge on the crucible and to the changes caused by the deoxidizers and other added materials makes it impossible to know the final composition of the product from the charge used.

Therefore, the exact composition of the alloy must be determined by analysis before it can be intelligently altered and the desired properties obtained.

Mr. C. W. Sievert* of the University of Illinois, with

* Senior Thesis, 1914)

this end in view, attempted a quantitative analysis of some of the samples and in doing so, encountered unexpected difficulties.

He found the extreme complexity of the alloy made it very hard to get a complete separation of the metals using the more common combinations of methods. Consequently, he set about comparing various methods of analysis for the purpose of formulating a scheme by which not only this alloy but all alloys of this type could be analyzed quantitatively.

The scheme that he devised although meeting part of the difficulties did not seem to give as concordant results as should be expected and failed to provide for the determination of all of the elements present in the various alloys. Therefore, this piece of work was attempted as a continuation of Mr. Sievert's work and to revise his scheme, if possible, so that concordant and complete quantitative results might be obtained on the various samples, thereby throwing some light upon the elements that materially alter the properties of the alloy.

The points of weakness in Mr. Sievert's scheme were determined by a series of analyses and it is our purpose to strengthen these by substituting other better adapted methods. The methods to be submitted have been tested by a series of determinations on a given sample and then on samples of different compositions so as

to insure their adaptability.

As a result of Mr. Sievert's work he formulated the scheme of analysis given in Plate I. The earlier part of the present work was carried on with him and in accordance with his scheme, which after repeated trial, seemed defective in a number of points as follows:

First, the impossibility of obtaining complete separation of the elements precipitated by hydrogen sulphide in alkaline solution even after a long series of repeated precipitations.

Second, losses resulting from excessive number of precipitations with ammonium hydroxide.

Third, the precipitation of manganese along with chromium and aluminum by ammonium hydroxide.

By a series of determinations by this outline, the following results were obtained showing the inaccuracy of the method.

Alloy No.64

	<u>Amount used</u>	<u>Determination by author</u>	<u>By Mr. Sievert</u>
Ni	66.66 %	56.8 %	63.52 %
		62.75	
		51.5	
Mn	1.4 %	None	.91 %
Cr	18.00 %	18.97	14.57 %

This particular alloy contained no cobalt.

From the above results we can readily see that the separation was not reliable under the conditions used and did not give concordant results.

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TABLE I. SCHEMATIC DIAGRAM OF SEPARATION.

Alloy, — may have following elements present. Ni, Co, Cr, Cu, W, Mo, Al, Ti, Mn, Si, Fe (B, C)

Dissolve in HCl. Evaporate. Add HCl and HNO_3 , evaporate. Add HCl, evaporate, finishing with a little HNO_3 . Add 5 cc HCl. Boil with 150 cc. of water.

<p><u>PRECIPITATE.</u> Si, W. Ignite in crucible. Add H_2SO_4. Evaporate. Weigh. Add $\text{H}_2\text{SO}_4 + \text{HF}$. Evaporate. Weigh. Difference = SiO_2</p> <p><u>RESIDUE</u> WO_3 Fuse with Na_2CO_3. Dissolve in water. Precipitate as benzidine tungstate. Weigh as WO_3.</p>	<p><u>SOLUTION.</u> Heat, pass in H_2S in a stoppered flask until cold.</p> <p><u>PRECIPITATE</u> Cu, Mo. Add $\text{NaOH} + \text{Na}_2\text{S}$ in a pressure flask. Heat on water bath filter.</p> <p><u>PPT.</u> CuS Add HNO_3. Determine by iodide method (Lew)</p> <p><u>Solution</u> Mo, as sulfo salt. Add H_2SO_4</p> <p><u>PPT.</u> MoS_3 Dissolve in HNO_3. Add NaOH. Determine as PbMoO_4</p>	<p><u>Solution.</u> Boil to expel H_2S. Add bromine water. Expel by boiling. Add $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$, boil, filter.</p> <p><u>PRECIPITATE</u> Cr, Al, Ti, Fe. Traces of Ni, Co, Mn. Dissolve in HCl. Repeat precipitation</p> <p><u>PRECIPITATE.</u> Cr, Al, Ti, Fe very little Ni, Co, Mn. <u>Solution.</u> Dissolve in HCl. Add NaOH and bromine water. Heat to boiling. Add Br_2 water. Black ppt. forms.</p> <p><u>PRECIPITATE</u> Ni, Co, Mn, to, Fe. Dissolve in HCl. Add to solutions A and B. <u>Solution C.</u></p> <p><u>SOLUTION.</u> Cr and Al as sodium salts. Add HCl until acid. Then add NH_4OH and boil.</p> <p><u>PRECIPITATE</u> Al. A small amount of Cr is also present. Dissolve in HCl and re-precipitate. If impure fuse with Na_2CO_3. Extract with water. Add HCl and NH_4OH. Ignite and weigh as Al_2O_3.</p> <p><u>SOLUTION.</u> Cr. Pass in H_2S until reduced. Add NH_4OH and boil off excess. Filter, ignite and weigh as Cr_2O_3.</p>	<p><u>Solution A.</u> Ni, Co, Mn. <u>Solution B.</u> Ni, Co, Mn. <u>Solution C.</u> A+B+C, containing Ni, Co, Mn, Ti, Fe. Make alkaline with NH_4OH. Acidify with acetic acid. Boil.</p> <p><u>PRECIPITATE</u> $\text{Ti}(\text{OH})_4$ A small amt. of iron may be present. Dissolve and add citric acid. Reppt. $\text{Ti}(\text{OH})_4$ with acetic acid or with NH_4OH. Ignite and weigh as TiO_2. Evaporate iron residue. Ignite to destroy citric acid. Fuse with KH_2SO_4 to bring it to solution.</p> <p><u>SOLUTION.</u> Add NH_4OH and NH_4Cl. Filter as soon as possible. Redissolve ppt. and repeat ppt., filtering immediately. Add second filtrate to first.</p> <p><u>PPT.</u> $\text{Fe}(\text{OH})_3$. Ignite and weigh or titrate with KMnO_4.</p> <p><u>PRECIPITATE</u> Ni, Co. Add KOH till alkaline. Acidify with acetic acid. Add KNO_2 slightly acid with acetic.</p> <p><u>Solution.</u> Add acetic acid. Pass in H_2S.</p> <p><u>Solution.</u> boil off H_2S. Precipitate in dilute H_2SO_4. Solution as $\text{MnO}_2 \cdot \text{H}_2\text{O}$. Dissolve in standard FeSO_4 solution. Titrate excess with KMnO_4.</p> <p><u>Precipitate</u> Co. as cobaltinitrite. Dissolve in HCl. Add NH_4OH and electrolyze. Weigh as Co.</p> <p><u>Solution</u> Ni. Add HCl. Boil to destroy nitrite. Make ammoniacal. Titrate aliquot portion with KCN.</p>

EXPERIMENTAL

After finding that the proposed method was inadequate the next step was to try some other mode of procedure. This was done by altering the scheme to the extent that the manganese was oxidized from the solution remaining after the hydrogen sulphide precipitation in acid solution, with potassium chlorate in concentrated nitric acid. This method gave very concordant results and shortened the analysis a great deal by reason of the fact that iron and titanium can be readily separated from the remaining solution: the former as the basic acetate and the latter as the hydroxide. This leaves in the solution only nickel, cobalt, chromium and aluminum. The chromium and aluminum can be readily separated from cobalt and nickel by oxidation with bromine in potassium hydroxide solution.

By using this revised plan the following results on alloy #82 were obtained:

Cr	22.85	Mn	1.45
	22.35		1.57
	22.66		
	22.85	Co	18.25
Ni	39.75		18.92
	39.11		
	39.11		
	39.57		
	40.51		

The above results seemed sufficient to justify both the use of the separation and the methods of determination as far as this particular sample was concerned. This was further proven by

running some complete analyses on other samples of the Parr alloy. The method as arrived at is more accurate than the Sievert method and much more rapid. A complete analysis can be run in about 40-50 hours barring accidents.

The accuracy and rapidity of the proposed method has been further substantiated by Mr. F. E. Rowland of the University of Illinois. He has worked in parallel with the author on the latter part of the work and his results are very consistent and check those of the author very closely.

METHOD OF SEPARATION

Solution of Sample.

The alloy, because of its acid resisting properties presents some difficulties in getting it into solution. Mr. Sievert found that aqua regia gave perhaps the most rapid solution under the following conditions:

A one gram sample is placed in a Jena glass evaporating dish, treated with 50 cc. of hydrochloric acid (Sp.Gr.1.19) and 15 cc. of nitric acid (Sp.Gr.1.42) and evaporated to dryness on the steam bath. The residue is treated with 5 cc. of hydrochloric acid (1.19) and again evaporated. After digesting the residue for two or three minutes with 50 cc. water and 5 cc. hydrochloric acid (1.12) it is allowed to settle and the solution decanted off. To the residue is added 5 cc. hydrochloric acid (1.19) and 2 cc. nitric acid (1.42), the solution evaporated to dryness, 2-3 cc. hydrochloric acid (1.19) added and the evaporation repeated. This residue after digesting with 50 cc. water and 5 cc. hydrochloric acid (1.12) is combined with the residue from the previous digestion and the whole filtered, giving solution (1). The precipitate or residue, which should be yellow in color, contains silica and tungstic oxide, both of which are insoluble in the acids used.

Treatment of Solution (1)

Solution (1) whose volume should now be about 125 - 150 cc. containing about 10-12 cc. hydrochloric acid (1.12) is saturated with hydrogen sulphide in a pressure flask, placed on the steam

bath and allowed to remain until the precipitate is completely settled. It is then cooled, filtered, and washed with a little hydrogen sulphide water containing a small amount of ammonium nitrate. (The precipitation is carried out in the pressure flask, as molybdenum if present, is more completely precipitated under pressure. The hydrogen sulphide water is used for washing instead of pure water as it prevents the oxidation of the precipitate while filtering. The ammonium nitrate is added to the wash water to coagulate any colloidal particles that may be in the solution and would otherwise run through the filter.) This precipitate is copper sulphide and molybdenum sulphide while the solution contains the remaining elements and is solution (2).

Separation of Copper from Molybdenum.

The sulphide precipitate of copper and molybdenum is treated in a pressure flask with dilute sodium hydroxide and a small amount of sodium sulphide (proportional to the amount of molybdenum in the precipitate), diluted to about 100 cc. and heated on the steam bath until solution of the molybdenum seems complete. This treatment dissolves the molybdenum sulphide, the soluble sodium sulpho-molybdate being formed, leaving the copper as the unchanged sulphide precipitate, which may be easily filtered off. By acidifying the sodium sulphide solution with sulphuric acid and heating in a pressure flask on the steam bath the molybdenum may again be precipitated as molybdenum sulphide.

Treatment of Solution (2)

Solution (2) is boiled to expel the hydrogen sulphide and

finally evaporated to 4 or 5 cc. 3 to 5 cc. nitric acid (1.42) are added and the solution boiled as long as oxides of nitrogen escape. 30 cc. of nitric acid (1.42) are then added, the mixture heated to boiling and treated with potassium chlorate in small portions until there seems to be no further precipitation. (This will probably require from one half to one gram depending upon the amount of manganese in the sample). When precipitation seems to be complete the solution is boiled for a few minutes and the beaker then placed in cold water. The manganese is completely precipitated as hydrated manganese dioxide, a dark brown precipitate. It is filtered through a Gooch filter, washed with a few cc. concentrated nitric acid that has been previously boiled with a little potassium chlorate to remove the oxides of nitrogen and finally with a small amount of pure water.

Separation of Titanium and Iron.

The solution from the manganese separation is evaporated almost to dryness to drive off most of the acid, diluted to about 50 cc. and made alkaline with ammonium hydroxide. The alkaline solution is then treated with about 5 grams of ammonium acetate and 5 cc. glacial acetic acid and boiled. This precipitates the titanium as titanium hydroxide and the iron as the basic acetate. The precipitate is dissolved in HCl, made alkaline with ammonium acetate and a small amount of citric acid added after which the titanium is reprecipitated with acetic acid and ammonium acetate. The remaining solution containing the iron is evaporated to dryness to destroy the citric acid, fused with potassium acid sulphate, the melt dissolved in water, made alkaline with ammonium hydroxide and

the iron reprecipitated as the hydroxide.

Separation of Aluminum and Chromium.

The solution remaining after the precipitation of the titanium and iron is made alkaline with potassium hydroxide and treated with bromine water, oxidizing the cobalt and nickel to cobaltic and nickelic hydroxides, which are insoluble, while the chromium and aluminum remain in the solution as chromate and aluminate respectively. This procedure will give a complete separation, but in the presence of large amounts of nickel or cobalt it is much better to repeat the process at least once. After the completion of the oxidation the precipitate is filtered off and thoroughly washed. Ppt. (A), combined solutions from the oxidation is solution (3).

Treatment of Solution (3).

The alkaline solution is acidified with hydrochloric acid and ammonium hydroxide added until it smells strongly after shaking. The excess of ammonia is boiled off and the precipitate of aluminum hydroxide filtered and thoroughly washed. If after this treatment the precipitate appears green, it is dissolved in hydrochloric acid, made alkaline with potassium hydroxide, oxidized with bromine water and the aluminum again precipitated as before. The solution which may contain a small amount of chromium is added to the solution from the first aluminum precipitation. Care must be taken at this point that large amounts of silica have not been dissolved from the glassware and mistaken for aluminum.

Treatment of Precipitate (A).

The nickelic and cobaltic hydroxides are very hard to separate and as they can be determined in the presence of one another it seemed advisable to do so, rather than attempt the separation.

DETERMINATIONSilica and Tungsten.

The yellow residue containing silica and tungstic oxide together with the filter paper is placed in a weighed platinum crucible and ignited, one or two cc. of sulphuric acid added to destroy any organic matter and then ignited to constant weight. This residue is treated with 2-3 cc. hydrofluoric acid and 1-2 cc. concentrated sulphuric acid and again ignited to constant weight. The silica forms silicon tetrafluoride which is volatile, leaving in the crucible only the tungstic oxide from which the percentage of tungsten may be calculated. The difference in weight before and after treatment with the hydrofluoric acid gives the amount of silica.

If care has been exercised in the first evaporations and the residue washed free from foreign matter, this treatment will be enough. However, if the residue upon ignition gives a very black substance, it should be fused with sodium carbonate after the hydrofluoric acid treatment, and the melt dissolved in water. If a precipitate remains, filter it off and reject. The alkaline solution is just neutralized with hydrochloric acid and 10 cc. of one-tenth normal sulphuric acid added. The tungsten is then precipitated as

benzidine tungstate with benzidine hydrochloride, filtered from the cold solution after standing for sometime and ignited to tungstic oxide.*

* Treadwell & Hall, Quantitative Analysis, Vol.2, p.290.

Copper.

There exist many methods for the determination of copper of which the electrolytic is the most common. But as this takes so much time and apparatus, the titration method seems more feasible for commercial purposes and is probably as accurate. The titration with sodium thiosulphate proved very satisfactory and gave very consistent results. The procedure is as follows:

The copper sulphide precipitate is dissolved in dilute nitric acid and the solution filtered to free it from sulphur. It is treated with 2-3 cc. of bromine water and boiled until the bromine is expelled, this removes all the oxides of nitrogen that would otherwise interfere with the titration. The solution is then made alkaline with ammonium hydroxide and about 7 cc. glacial acetic acid and 12 cc. potassium iodide (400 grams per liter). The iodine liberated is then titrated with standard sodium thiosulphate.*

* Treadwell & Hall, Analytical Chemistry, Vol. II., p.682.

Molybdenum.

The precipitate of molybdenum sulphide is filtered through a Gooch crucible and thoroughly washed. It is then heated

in a covered crucible until all the excess sulphur is distilled off. During this heating the crucible must be covered, for at the temperature at which the sulphur will volatilize, it will also take fire and burn if exposed to the action of the air. This would cause an appreciable error due to the volatilization of the unoxidized molybdenum sulphide. When all the free sulphur is driven off most of the molybdenum will be oxidized to molybdic oxide, which can then be heated to a dull red heat for sometime to insure complete oxidation. It is then ignited and weighed as molybdic oxide, MoO_3 . The weight of molybdic oxide times .66667 is equal to grams molybdenum.

Manganese.

The hydrated manganese dioxide precipitate together with the Gooch crucible is placed in the beaker in which it was originally precipitated, (the same beaker being used to prevent the loss of any of the precipitate that might adhere to the sides of the beaker), and about 50 cc. of standard ferrous ammonium sulphate added. This is then shaken with glass beads until all of the precipitate has been dissolved, after which the excess ferrous ammonium sulphate is titrated with one-tenth normal potassium permanganate. One cc. equals .002747 grams manganese. *

* Treadwell & Hall, Vol. II., p.619.

Another method may be substituted for this which will eliminate the necessity of preparing the standard solutions for the first methods. The hydrated manganese dioxide precipitate may be treated with about 10-15 cc. of potassium iodide solution

(15 grams per liter) and 30-40 cc. of hydrochloric acid (1.12), the whole shaken until the precipitate is completely dissolved, diluted to about 150 cc. and the liberated iodine titrated with standard sodium thiosulphate solution.

Chromium.

The chromate solution is made acid with hydrochloric acid and a small amount of ethyl alcohol added, and the solution boiled to reduce the chromium to the chromic state. The boiling is continued until all the chromium is reduced as shown by the dark green color of the solution, and most of the aldehyde formed by the oxidation of the alcohol has been expelled. Ammonium hydroxide is then added in slight excess and the solution boiled until it no longer gives an odor of ammonia. The excess must be boiled off to insure complete precipitation, since the chromic hydroxide is soluble to a slight extent in excess of the reagent. Precipitation of the chromium by this method gives a very copious precipitate and one that is extremely hard to wash free from occluded salts. Therefore, to eliminate the possibility of contamination the precipitate should be washed as thoroughly as possible, dissolved in hydrochloric acid, and reprecipitated with ammonium hydroxide. The precipitate is filtered, washed, ignited wet and weighed as chromic oxide. The weight of the precipitate times .68421 equals grams chromium.

Aluminum.

The aluminum hydroxide may at this point contain quite an amount of silica acquired from the glass, which must of course be removed before the aluminum can be determined. Therefore, the pre-

precipitate is dissolved in hydrochloric acid, filtered, and the aluminum again precipitated with ammonium hydroxide. The precipitate is filtered off, ignited and weighed as aluminum oxide, Al_2O_3 . To be assured that all of the silica has been removed, the residue after ignition should be treated with a small amount of hydrofluoric and sulphuric acid evaporated, ignited and weighed. The weight of aluminum oxide times .53033 equals grams aluminum.

Nickel.

Due to the fact that nickel and cobalt are so difficult to separate, but may be determined in the presence of each other, the latter method is used. However, cobalt not being a very beneficial constituent of such alloys, nickel is more often found alone, and when so found a more rapid method may be used.

If there is no cobalt in the solution, the nickel may be easily and rapidly determined by titration with potassium cyanide in slightly ammoniacal solution.* In the titration, the sol-

* Treadwell & Hall, Quantitative Analysis, Vol. II., p.720.

uble complex potassium nickel cyanide is formed. The solution which should not contain more than one-tenth gram of nickel in 100 cc. of solution is made slightly alkaline with ammonium hydroxide. Five cc. of potassium iodide solution and five-tenths cc. of standard silver nitrate are added, the latter being accurately measured from a burette. This will give a precipitate of silver iodide which will not dissolve upon the addition of potassium cyanide until all of the nickel has been changed to the complex cyanide.

When cobalt is also present in the solution, the nickel may be determined by the dimethylglyoxime method.* The solution

* Treadwell & Hall, Quantitative Analysis, Vol. II., p.129.

which should not contain more than one-tenth gram of cobalt in 100 cc. is made neutral with potassium hydroxide. The theoretical amount of one per cent alcoholic dimethylglyoxime is added to the hot solution. Enough ammonium hydroxide is then added to give the solution a slight odor of ammonia. The carmine red precipitate which comes down immediately, is filtered in a Gooch crucible while hot, washed with hot water, dried at about 115° for about 45 minutes, and weighed. The precipitate is 20.31 per cent nickel. In case the theoretical amount of one per cent alcoholic dimethylglyoxime is more than 25 cc., an aliquot part of the solution should be used as the nickel dimethylglyoxime is soluble in excess of alcohol. Also care should be used in the addition of the ammonium hydroxide to the solution as an excess will tend to dissolve part of the precipitate.

Cobalt.

Cobalt may be titrated from the nickel solution by the method presented by A. Metzl (Z. Anal. Chem. 53; 537-41, 1914; Chem. Abs.9; 1, 40, 1915). A one-tenth aliquot part of the solution is treated with 10 cc. ammonium chloride (166 grams per liter) 10 cc. ammonium hydroxide (sp.gr. .9) and 7-10 cc. $\frac{3}{25\%}$ per cent hydrogen peroxide and heated for 10 minutes. 25 cc. of/potassium hydroxide is added, the solution boiled until the odor of ammonia disappears. Cooled, acidified 7-10 cc. potassium iodide (100 grams in 400 cc.) added and the iodine titrated with sodium thiosulphate

TABLE II

Take 1 gr. of alloy which may contain Si, W, Cu, Mo, Mn, Ti, Al, Cr, Co, Fe, and Ni
 Heat with 50 cc. HCl (1.19) and 15 cc. HNO₃ (1.12) Evaporate to dryness. Add 5 cc. HCl (1.19). Again evaporate.
 Digest with 50 cc. H₂O and 5 cc. HCl (1.12). Decant. Add to residue 5 cc. HCl (1.19) and 2 cc. HNO₃ (1.42). Evaporate to dryness. Add 5 cc. HCl (1.19). Again evaporate. Digest with 50 cc. H₂O and 5 cc. HCl (1.12). Filter combining the solution and residue with that of first digestion.

Residue SiO₂
 Page 10
 Page 10

Sol. (1) Page 6 Cu, Mo, Ti, Cr, Mn, Al, Co, Ni, as chlorides

Place in pressure flask, saturate with H₂S place on steam bath until precipitation is complete
 Filter, wash ppt. with H₂S water containing a little NH₄NO₃.

Ppt. = CuS and MoS₃
 Page 7 and 11

Sol. (2) Page 7 Mn, Ti, Cr, Al, Co, Ni, Fe, as chlorides

Evaporate to 2-3 cc. Boil with 5 cc. HNO₃ (1.42). Add 30 cc. HNO₃ (1.42). Heat to boiling, add about 1 gr. KClO₃. Boil. Filter through Gooch crucible.

Ppt. = MnO(OH)₂
 Page 12

Sol. Page 8 Ti, Cr, Al, Co, Ni, and Fe as nitrates

Evaporate to expel most of acid. Add 5 grms NH₄C₂H₃O₂ and 7-10 cc HC₂H₃O₂. Boil. Filter wash ppt. with H₂O

Ppt. Ti(OH)₄ and
 Fe(OH)(C₂H₃O₂)₂
 Page 8

Sol. Page 9 Cr, Al, Co, and Ni.

Make alkaline with KOH. Add Br water. Boil.
 Filter and wash.

Ppt. Page 9 Co, Ni and some Cr.
 Dissolve in HCl, add KOH, Br
 water. Boil, filter and wash.

Sol. (3) Page 9

Evaporate to about 250 cc.
 Make acid with HCl and alkaline
 with NH₄OH. Filter and wash
 precipitate.

Ppt. (A) Co and Ni Sol.
 Repeat oxidation if necessary
 and add solution to Sol. (3)

Ppt = Al(OH)₃
 Page 13

Sol. Page 12 Cr
 Acidify with HCl add
 C₂H₅OH and Boil. Make
 alkaline with NH₄OH
 Boil, Filter and wash

Ppt Cr(OH)₃
 Page 13

Sol. = waste
 salts
 Destroy

using starch indicator.

RESULTS

By following the scheme of analysis that has been described and given in brief in Plate II., the following results were obtained. Mr. Rowland has kindly consented to the use of his results on some of the same alloys as a check on those of the author.

Table No.1

Results of Silicon and Tungsten determinations.

Alloy No.82

<u>Si</u>	<u>W</u>
1.61 -----	4.33
1.58 -----	4.45
1.60 -----	4.65
1.41 -----	3.64 ?
1.58 -----	3.36 ?

Alloy No.117

<u>Results by author</u>		<u>Results by Mr.Rowland</u>	
<u>Si</u>	<u>W</u>	<u>Si</u>	<u>W</u>
1.38 -----	.48 ?	1.05 -----	2.16
		1.03 -----	2.09

Alloy No.120

<u>Results by author</u>		<u>Results by Mr.Rowland</u>	
<u>Si</u>	<u>W</u>	<u>Si</u>	<u>W</u>
1.015	2.30	.99	2.50
.97	2.94		

Table No.2

Results on Copper and Chromium determinations

Alloy No.82

<u>Cu</u>	<u>Cr</u>
9.45 -----	22.85
10.06 -----	24.63
10.06 -----	22.36
10.41 -----	22.66
10.39 -----	22.85
	22.27
	21.80

Alloy No.117

Results by authorResults by Mr.Rowland

<u>Cu</u>	<u>Cr.</u>	<u>Cu</u>	<u>Cr</u>
7.32 -----	21.07	6.34 -----	18.75 (low)
7.90 -----	19.77 ?	6.51 -----	

Alloy No.120

Results by authorResults by Mr.Rowland

<u>Cu</u>	<u>Cr</u>	<u>Cu</u>	<u>Cr</u>
7.55 -----	23.19	7.49 -----	23.43
7.44 -----	23.42		

Table No.3

Results of Ni, Al, Mn, Fe and Co determinations
Alloy No.82

<u>Ni</u>		<u>Fe</u>		<u>Al</u>
39.75	-----	None	-----	.49
39.11	-----			
39.11	-----	Mn	-----	Co
40.51	-----	1.57	-----	18.92
39.57	-----	1.45	-----	18.25

Alloy No.117

Contained no Co or Fe

Results by author

Results by Mr.Rowland

<u>Ni</u>	<u>Al</u>
61.37	.78 ?
60.50	1.12

<u>Ni</u>	<u>Al</u>
60.65	1.09

<u>Mn</u>	<u>Mn</u>
3.03	.98
3.02	.98

Alloy No.120

Contained no Co

<u>Ni</u>	<u>Al</u>	<u>Bi</u>	<u>Al</u>
60.15	2.01	60.28	1.54
58.06	2.04		
<u>Fe</u>	<u>Mn</u>	<u>Fe</u>	<u>Mn</u>
.60	.90	.75	.84
.47	.89		

Table No.4

Showing complete analysis of Alloy No.82

	Put in (approx.)			<u>Found</u>		
Cu	-----	10.00	-----	10.07	average of 5	
Si	-----	1.50	-----	1.60	"	" 4
W	-----	4.50	-----	4.47	"	" 3
Ni	-----	40.00	-----	39.61	"	" 5
Al	-----	1.00	-----	.49		
Cr	-----	20.00	-----	22.77	"	" 7
Mn	-----	.70	-----	1.51	"	" 2
CO	-----	21.00	-----	18.45	"	" 2
Mo	-----	<u>.30</u>	-----	<u>None</u>		
Total		99.00	-----	99.06		

Table No.5

Showing complete analysis of Alloy No.117

	Put in		<u>Found</u>	
			<u>By author</u>	<u>By Mr.Rowland</u>
Cu	----	6.6	7.61	6.42
Mn	----	1.25	3.02 ?	.98
Si	----	.40	1.38	1.04
W	----	2.00	.48	2.13
Ni	----	62.00	60.93	60.65
Al	----	1.50	.92	1.09
Fe	----impurities	---	none	.76
Cr	----	21.00	21.07	18.75 (low)
MO	----	6.00	2.43 (low)	4.67
Insoluble	-----	-----	<u>1.98</u>	<u>none</u>
Total		100.75	99.82	96.49

Table No.6

Showing complete analysis of Alloy No.120

	Put in		Found	
			<u>By author</u>	<u>By Mr,Rowland</u>
			(Average of 2 analyses)	
Cu	-----	7.50	----- 7.50	----- 7.49
Mn	-----	1.00	----- .90	----- .84
Si	-----	.50	----- .99	----- .99
W	-----	3.00	----- 2.62	----- 2.50
Ni	-----	63.00	----- 60.56 (one det.)	60.28
Al	-----	2.00	----- 2.02	----- 1.54
Fe	-----	impurities	--- .53	----- .75
Cr	-----	<u>25.00</u>	----- <u>23.30</u>	----- <u>23.43</u>
		102.00	98.42	97.82

DISCUSSION OF RESULTS

Silicon.

The silicon determinations seem very consistent in all cases. Those of the author were checked very closely by Mr. Rowland.

Tungsten.

In some of the tungsten determinations the results do not seem to check as well as should be expected. In Table No.1, the per cent of tungsten as found by the author shows only 0.48% while Mr. Rowland's determinations show 2.12% and the amount added was approximately 2.00%. By referring to Table No.5, we note that the author has obtained 1.98% of residue insoluble in acids or by fusion with sodium carbonate, which in all probability accounts for part of the wide variation. In working with this residue Mr. Rowland found it contained traces of nickel and chromium. With this exception, for which we have accounted in part, the results check as closely as could be expected.

Chromium.

The chromium determinations seem to agree very well in all cases. However, in the analysis extreme care must be used in washing the chromic hydroxide to completely remove any occluded salts.

Aluminum.

The aluminum determinations do not check as well as should be expected. However, with the large amounts of nickel and chromium present, it is not surprising that poor checks were obtained. But with the results of the aluminum determinations on Alloy No.120 (Table No.3) it is evident that most of the points of

error have been eliminated.

Manganese.

With the exception of the difference between the check results of the author and Mr. Rowland on Alloy No.117 (Table No.3) the manganese results seem very good, but in this case the author's results seem very high which was probably due to the different method of final determination used.

Complete Analysis.

Tables Nos.4, 5, and 6 show that in every case the sum of all the elements determined in the complete analysis is less than one-hundred per cent. Part of this difference, however, can be accounted for by the fact that the alloys contain at least a small amount of carbon which was not determined. The remaining difference is probably caused by errors in manipulation on such a long analysis.

For the most part, the percentages check the amounts put in very closely, but they cannot be expected to check exactly as the percentages put in are approximations, because some scrap from previous fusions were used and because of the slight change in composition during fusion as before described.

In most cases the silicon determinations are higher somewhat than the amount added, the difference being due to the absorption of small amounts of silica from the flux.

CONCLUSIONS

In concluding we feel that we have formulated a scheme whereby the composition of complex alloys of this type can be determined with a reasonable degree of accuracy.

From the results of the analysis we have also shown that the composition of the product is not very different from that before fusion, the greatest differences being in those metals that are added in the largest proportions, as would ordinarily be expected.

OTHER EXPERIMENTAL RESULTS

At the suggestion of Professor Parr some analyses were run on some commercial alloys used for ignition points on gas engines; namely, "Meteor Wire" and "Platin Draht".

Results were obtained as follows:

Meteor Wire

Ni	-----	91.51	-----	91.61
Fe	-----	.50	-----	.50

Platin Draht

Ni	-----	97.86	-----	97.88
Fe	-----	.88	-----	.87
Mn	-----	.36	-----	.40
Mo (estimated).	.50	-----		.50

Although the results on the "Meteor Wire" show only a 92% total, a very careful qualitative test was carried out, but no other elements were to be found.





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